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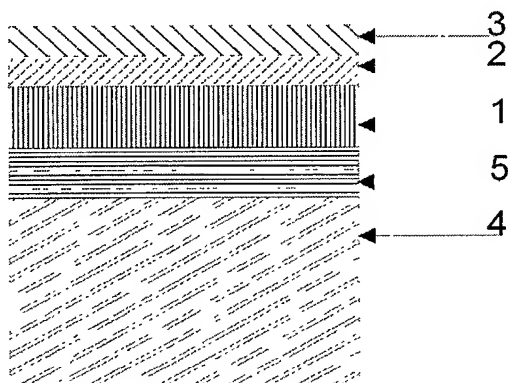
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(54) Title: DRY MULTILAYER INORGANIC ALLOY THERMAL RESIST FOR LITHOGRAPHIC PROCESSING AND IMAGE CREATION



(57) Abstract: A thermal inorganic resist useful for lithographic processes and image creation is created by depositing on a substrate at least two layers of materials which are typically metals. The materials form a mixed alloy with a eutectic. One embodiment has a 15 nm Bi layer overlying a 15 nm In layer. Upon exposure to a optical light pulse of sufficient intensity, optical absorption heats the layers above the eutectic melting point (110° C for BiIn) and the resist forms an alloy in the exposed area. By selectively heating parts of the resist a desired pattern can be created in the resist. Optical characteristics of the alloyed layers are typically different from those of the unexposed layers. In BiIn resists the alloyed areas are visually transparent compared to the unexposed sections. The exposed pattern provides a viewable image useful for exposure control. In a negative resist the alloy material is resistant to development etches which remove the unexposed areas but only slowly etch the alloyed areas creating a lithographic structure. This

resist structure can be used to pattern layers below it in additional etches. The resist layer can then be stripped, leaving the pattern layer on the substrate. In resists showing significant optical differences (such as BiIn) after exposure this same material can be used to create images for data storage, and, when transparent, photomasks for optical lithography.



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**DRY MULTILAYER INORGANIC ALLOY THERMAL RESIST FOR  
LITHOGRAPHIC PROCESSING AND IMAGE CREATION**

Cross-Reference to Related Application

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This application claims the benefit of the filing date of United States patent application No. 09/618,065 filed July 17, 2000.

Technical Field

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This invention relates to multilayered inorganic films which can be imaged thermally to create structures for patterning layers. The invention is applicable both to lithographic processes, such as those used in integrated circuit fabrication, and the making of images in thin films, such as is required in creating optical masks.

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Background

Integrated circuit and semiconductor devices are built using microfabrication lithographic techniques to pattern many layers of conductors, insulators and/or semiconductors. In lithography a masking layer, called a resist, is deposited on a substrate and exposed by projecting an image onto its surface. The exposure changes properties of the resist. For optically sensitive resists (photoresists) a chemical reaction occurs in portions of the resist which are exposed to light.

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Typically, after development, the exposed areas are removed. Unexposed areas remain creating a raised pattern of resist on the surface (a reverse or negative resist process is also possible). This raised pattern protects parts of underlying layers so that when exposed to an etching environment (for example acids, etching gases or plasmas or ion beams) the protected parts of the underlying areas are protected from etching, while those parts of the underlying layers which are not covered by resist are preferentially removed. The resist layer is then stripped or removed leaving a transferred raised pattern from the mask in the layer on the substrate. The patterned layer may be used directly as defined or in turn may be used to pattern a layer below it on the substrate, either for additional etching processes, or other operations (for example creating doped patterns with impurities, or growing patterned oxide layers). Repeated processes of layer deposition and lithographic patterning can be used to create everything from simple single layer structures to complex integrated circuits.

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5 Photomasks used in optical lithographic processes are typically themselves created by directly writing with a focused laser or electron beam spot a pattern into a resist on an optically transparent substrate, usually coated with a thin absorbing layer. That resist pattern then defines the etching of the lower layer, patterning the absorbing and non-absorbing areas on the transparent substrate creating the mask used in other lithographic processes.

10 Current lithographic processes typically use organic based photoresists which are typically applied as liquids to a substrate or wafer. The substrate is then spun at high speeds so that interaction of rotational, gravitational forces, surface tension and viscosity creates a film resist having a desired thickness. The film is then baked to remove solvents before the photolithographic exposure. The photoresist is then developed using a wet chemical processes that removes unwanted resist. After the lithographic etching processes the remaining photoresist is stripped (often in an oxygen plasma etcher or with liquid strippers).

20 It is very hard to remove all the organic materials resulting from the application of the resist, and there is always the danger of other outside contaminants. Typically very aggressive chemical cleaning processes, such as the industrial standard RCA clean, must be used to remove organic materials after an organic-based resist has been used. Such cleaning processes are very time, energy and material consuming. Resist contamination is a common source of defect creation in integrated circuit processes.

25 In addition to contamination problems organic resists are very wavelength sensitive. Typical optical exposure systems use ultra violet (UV) excimer lasers operating at 248 nm wavelength as the light source. These lasers produce short (5-20 nsec.) high power pulses to create the small structures needed. Resists designed for exposure by the currently-used 248 nm wavelength will not work with future exposure systems which may use 193 nm, 150 nm or even shorter wavelengths to make structures smaller than 0.1 microns. Furthermore, at shorter wavelengths and high power pulses many organic resist materials are damaged (photoablated) because the energy of the UV light causes organic molecules to decompose. This photoablation can result in ablated materials being deposited on the exposed optics.

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An inorganic-based dry resist processes could provide significant advantages. Firstly, a dry process using an inorganic resist would allow patterned resists to be applied mostly in a vacuum environment. This would allow transfer from a dry based deposition of a layer (for example by sputtering) to the dry  
5 inorganic resist coating, to the exposure, etching (for example, plasma etching) to the resist stripping processes. Performing more processes in a vacuum environment provides reduced opportunity for contamination, and hence potentially would reduce the rate of defects. Secondly the use of a resist which does not include organic materials may significantly reduce the number of cleans needed in process steps with  
10 resulting savings in time, materials and energy. Thirdly many inorganic resists are thermally activated. Thermal resists, especially those using metal-based inorganics, can be less wavelength sensitive and may operate at very short wavelengths. Fourthly metal-based inorganics can avoid the photoablation effect down to very short wavelengths. Fifthly thermally reacted inorganics can show different optical  
15 characteristics after exposure than before. Thus the exposed areas can be identified before the development processes. This allows errors in exposure to be corrected.

Gelbart and Karasyuk have shown that with thermal resists and a special multiple exposure modification existing optical exposure systems can be used to  
20 make structures smaller than is possible with conventional optically exposed resists. Current exposure systems are diffraction limited by their optics and need to use shorter wavelengths (193 nm and 150 nm) to pattern structures below 0.1 to 0.07 microns. However Gelbart and Karasyuk show that by use of a multiple exposure modification to existing (248 nm) systems resolution below 0.1 microns may be  
25 possible and below 0.1 micron with shorter wavelengths. This multiple exposure system requires resists that do not follow the law of reciprocity. The law of reciprocity says that total exposure is integrated over time, meaning that two exposures at half-threshold produce the same exposure as one exposure at full threshold. Thermal resists react when the resist is heated above a certain  
30 temperature and do not follow the law of reciprocity. Thus, if a thermal resist is heated to just below the threshold, allowed to cool, and then heated a second time to the same point, it will remain unexposed. In a microfabrication exposure system, the UV light arrives in pulses of a few tens of nanoseconds spaced hundreds of  
microseconds apart. This means that there is sufficient time for the material to cool  
35 between UV exposures. By comparison standard photoresists follow the law of reciprocity and a multiply exposure system produces the same result as a regular exposure.

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While thermal inorganic resists offer certain advantages, previous attempts to provide such resists have encountered significant problems, especially with their sensitivity. Janus, U.S. patent No. 3,873,341, proposes an amorphous iron oxide based film as a thermal resist. When heated by an optical exposure system the amorphous iron oxide becomes crystallized if the local temperature exceeds 820°C. The crystallized iron oxide areas are attacked by acid more rapidly than the amorphous, and hence can be selectively removed. However, this high threshold temperature requires unacceptable exposure light intensities in current optical exposure systems.

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Bozler et al., U.S. patent No. 4,619,894 discloses another thermal inorganic resist consisting of an aluminum film deposited in a low-pressure oxygen atmosphere. This creates an aluminum oxide cermet. When exposed to a UV laser pulse the cermet is converted from a conductive phase to a highly resistive oxide phase. This resistive material is also etched at a much lower rate by a phosphoric acid etch than the cermet, thus creating the desired resist structure. While the optical exposure required by the cermet resist is 1000 times less than the Janus resist, it still requires temperatures in the 300°C range, and thus exposures 4-10 times greater than current resists, requiring 40 to 100 mJ per square cm of UV light in the 20 nsec laser pulse. Current resists require about 10 mJ per square cm per pulse of UV light for exposure. Both the Janus and Bozler thermal inorganic resists are too insensitive for most applications. Neither discusses how the resist can be stripped. Removal of Bozler's patterned cermet resist without damage to some metal layers below would be difficult.

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Using lasers to alloy film layers and alter their reflectivity is well known in the creating of optical writeable disks for information storage. In particular Takeuchi et al., U.S. patent No. 5,851,729, describes a system using a Bismuth-Tellurium Bi-Te alloy layer that is sandwiched between two Antimony-Selenium Sb-Se films. When hit with a laser the 3 layers alloy to create a Bi-Te-Sb-Se film with different reflectance from that of the unalloyed layer. Nakane in U.S. patent 4,587,533 teaches another optical write alloying system using a transparent upper layer with a lower melting temperature lower metal layer of Te, Bi, Sb or In. The laser light passes through the upper layer, and melts the lower layer which alloys with the transparent upper layer to significantly change the materials' reflectivity. However while Takeuchi, Nakane and others teach the multilayer alloying concept they focus is on creating alloys whose optical

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characteristics, especially their reflective, substantially changes from the unexposed to alloyed state. The relative etching rate of the unexposed and alloyed areas is not considered or discussed as important in their choice of materials. For a workable thermal resist for microfabrication needs the change in the optical characteristics is of much less importance than the etch ratio of the unexposed and alloyed films. Optical changes would be useful to identify the exposed area before development, but it is not necessary for a successfully functioning thermal resist. Optical changes may be useful in some applications like creating photomasks.

10 In addition the optical writeable disk technologies all require that the unexposed multilayers not be alloyed by the laser beams reading the disk information. Since these reading lasers are typically 1-2 mW of laser light focused to spots of less than one micron this requires a significant thermal threshold (typically more than 250-400°C) before the alloying can occur. However good thermal resists require the opposite condition: the lower the thermal reaction temperature the more sensitive to illumination is the resist making it more desirable. Indeed the exposure induced by the optical writable disk readout laser is typically in the 400,000 W/sq cm range making it that of current photolithographic exposure systems. Thus the alloys and processes best for optical disk writing are poor candidates for thermal inorganic resists just on thermal energy considerations.

25 In addition they are specific to particular materials and thus hard to modify to improve the process. There remains a need for inorganic thermal resists that may be used in lithographic processes. There is a particular need for such resists that have both good sensitivity (UV exposure requirements) and are compatible with current integrated circuit contamination requirements.

#### Summary of the Invention

30 Illustrative embodiments of the present invention are described in the following detailed description. This invention relates to a class of dry inorganic thermal resists based on a multilayer process. In its simplest form the thermally active layer consists of two layers of inorganic materials which are usually single element metals or binary metal alloys. A lower thin film of one inorganic material (in one example an Indium (In) film) underlies an overlying thin film of another inorganic material (in one example a Bismuth (Bi) film). The materials of the layers have a low temperature alloy, a eutectic, whose melting point is below that of the

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materials of either of the two individual films. Best results occur for eutectic temperatures below 300°C and preferentially below 200°C, with temperatures in the 100°C or below being possible with some alloys. More complex embodiments of the invention may comprise more than two layers.

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Accordingly, one aspect of the invention provides a thermal inorganic resist comprising: a first layer of a first material on a substrate; and a second layer of a second material on the first layer. The resist is characterized by the first and second materials having a eutectic alloy and the first and second layers having thicknesses  
10 such that alloying the materials in the first and second layers results in a composition near that of the eutectic alloy. Preferably the composition is within a few percent (for example,  $\pm 10\%$  more preferably  $\pm 5\%$ ) of that of the eutectic alloy.

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Another aspect of the invention provides methods for providing a thermal inorganic resist. The methods comprise depositing a first layer of an inorganic thin film on a substrate; depositing one or more layers of another inorganic material or materials on the first layer; and imagewise exposing the layers to create a resultant material. In various embodiments of the invention the resultant material has  
20 different etching characteristics from the unimaged material; a melting point below those of the materials of the first layer and one or more additional layers; and/or has optical characteristics different from any of the unexposed materials thus creating a visible image on a surface of the resist which can be viewed by simple illumination with optical radiation.

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Yet another aspect of the invention provides a photomask comprising at least two layers of thin inorganic coatings. The coatings changing from opaque to transparent when heated.

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Optical absorption characteristics of the films determine the combined layer thickness and the order of the layers. The order of which material is on the top layer is preferably selected to provide a minimum reflection and maximum absorption. For proper choice the material's optical index of refraction and absorption index at the desired wavelengths should be calculated to obtain these.

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Total film thicknesses are best when the optical energy absorption rate allows energy deposition in both film layers. As many films are highly absorbing metals calculations must be done using optical multilayer thin film analysis including



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complex indexes, and Poynting vector analysis, both including the effects of internal reflections. In general the actual energy deposited in the film per unit volume increases as thickness decreases, resulting in more sensitivity for total film thicknesses less than 70 nm. The films are in general only modestly wavelength sensitive. For some metal films the wavelength range of successful operation tested has ranged from the near infrared (860 nm) to UV (266 nm). There are however different exposure requirements at different wavelengths. While films less than 70 nm provide best sensitivity thicker films (up to at least 300 nm) show the same alloying effects, but required more laser power.

The underlying film may be deposited via a dry process (for example sputter deposition or CVD deposition). The overlying layer may be deposited by the same process, preferably in the same deposition system.

While an alloying action is the simplest, some alloys may also combine with oxygen, nitrogen or hydrogen to form films with significantly different characteristics than both the thin layer materials or their oxides, nitrides or hydrides. This may occur either with gases in the atmosphere above the films during exposure, or from atoms trapped in the film during deposition, or even from layers that are oxides to begin with (usually the bottom layer).

The desirable post-alloying characteristics are application-dependent. Most useful materials show a significant optical change between the alloyed and non-alloyed areas. Depending on the materials used alloyed films range from little optical change to significant increases/decrease in reflectivity or colour to films. Optical transmissions may significantly decrease, and in some tested cases actually go from nearly completely absorbing in the unexposed case to almost completely transparent in the alloyed case (as in the case of one embodiment, BiIn, films showing such changes). Films that alloy and show a substantial decrease in absorption may be used to directly write optical images photomasks for some applications.

The development etching characteristics of the alloyed layer in some materials are very different from the unalloyed material. General results have shown the alloyed material is much more resistant to etching than the unexposed layers. Etching rate ratios of alloyed to unexposed will depend on the specific etchant and etching processes used (for example wet acids or dry plasma). With

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some alloys (as in BiIn) a simple wet etchant will remove the unalloyed layer, leaving the alloyed layer. This development etch generally results in a negative thermal resist with the alloyed areas left behind and the unexposed areas removed.

- 5           The thermal inorganic resist layers are very thin (typically 30 – 70 nm). Also they are not resistive to all etchants needed for all commonly used layers on the substrate. In most applications an inactive protection layer is deposited before the multilayer resist is deposited. After the patterning exposure and development etch of the multilayer inorganic resist it acts as a mask layer for the protection layer.
- 10   Protection layers are chosen to have a significantly different etch characteristic to that of the alloyed resist. For example in the case of metal multilayers a thick (about 1 micron) layer of carbon is currently preferred. An oxygen plasma development etch would in many cases remove the carbon without attacking the alloyed resist. This leaves a multilayer developed resist consisting of the alloyed
- 15   resist and protection layer. This provides significantly better protection for etching many of the lower layers.

- To work in any microfabrication process a resist must be easy to strip or remove, leaving the substrate clean of any remnant resist or contamination, but
- 20   without damaging any of the layers below. This is especially important for reworking a resist definition that has defects in it. A microfabrication standard cleaning processes etch (RCA 2 or HCl: H<sub>2</sub>O<sub>2</sub>: H<sub>2</sub>O in the ratio 2:3:14) has proved successful in stripping the thermal inorganic resist in one case (BiIn). Dry etches or ion milling can also be used as the layer is very thin. The protection layer can be
- 25   removed with a dry etch (Oxygen plasma in the case of a carbon layer). This will leave a clean substrate ready for the next processing step.

- Since more than one material combination has successfully shown some or all of these characteristics this patent discloses a general class of inorganic thermal
- 30   resists that have low temperatures of conversion, form alloys over a wide wavelength range, do not show ablation of materials after exposure, show significant different optical parameters from the unexposed areas after the exposure allowing the patterning to be determined before development, more than one material is transparent after exposure making them candidates for optical masks,
- 35   and some show a significant etching difference between the alloyed and unexposed materials allowing a development etch to pattern the layer, and yet have a simple resist strip.

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Further features and advantages of the invention are described below.

#### Brief Description of the Drawings

5 In figures which illustrate non-limiting embodiments of the invention:

Figures 1A through 1D are partial schematic cross sections of a substrate during deposition steps in the creation of a thermal inorganic resist having a lower protection layer according to one embodiment of the invention which could be used in photolithography or mask creation;

10 Figures 2A through 2C are partial schematic cross sections of a substrate during deposition steps in the creation of a thermal inorganic resist according to another embodiment of the invention in which there is no protection layer;

Figures 3A through 3G are schematic cross sections illustrating the structure of a device at intermediate points during a photolithographic process using the resist  
15 of Figure 1;

Figure 4A through 4D are schematic cross sections illustrating the structure of a device at intermediate points during a photolithographic process using the resist of Figure 2;

20 Figures 5A and 5B are partial schematic cross sections of the substrate and resist of Figure 2 during a direct laser write process which will pattern the resist with exposure and a development etch;

Figure 6 illustrates for one embodiment of the resist of Figure 1 the calculated variation with resist thickness of the optical reflectivity, energy absorbed in the resist, and the light transmitted through the resist; and,

25 Figure 7 illustrates a calculation of the energy deposition with depth in one embodiment of the inorganic thermal resist of Figure 1.

#### Description

30 The invention will now be described with reference to the drawings in which the reference numbers designate similar features. As shown in Figures 1A to 7 this invention provides a general class of dry multilayered inorganic thermal resists.

35 In its simplest form the thermally active layer has a lower thin film of one inorganic material, usually a single element metal or a binary metal alloy (in one example an Indium film) and an overlying second layer of another inorganic material. The second layer is also commonly a single element metal or a binary metal alloy (in one example a Bismuth film). In more complex embodiments of the

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invention there may be more than two layers. The materials that are potential candidates for the two or more layers are those which show in their phase diagrams a low temperature alloy, a eutectic, whose melting point is below that of the two individual layers. Best results occur for eutectic temperatures below 300°C and preferably below 200°C, with several good materials near 100°C or below. Note some phase diagrams show more than one phase material ratio with temperatures below the individual layer melting points.

Candidate binary metal thermal resist are given in Table I which contains data taken from phase diagrams in Hansen.

TABLE I				
	Eutectic 1		Eutectic 2	
Elements	Temperature °C	Composition	Temperature °C	Composition
AsPb	288	7%As		
BiCd	144	45%Bi		
BiCo	258	90%Bi		
BiIn	72	22%Bi	110	53%Bi
BiPb	125	56%Bi	184	36%Bi
BiSn	139	43%Bi		
BiZn	254	92%Bi		
CdIn	123	74%In		
CdPb	248	72%Pb		
CdSb	290	7%Sb	445	57%Sb
CdSn	177	67%Sn		
CdTi	203	72%Ti		
CdZn	266	26%Zn		
Galn	16	16%In		
GaMg	285	67%Ga	422	19%Ga
GaSn	20	5%Sn		
GaZn	25	5%Zn		
InSn	117	47%Sn		
InZn	143	7%Zn		
MgPb	253	85%Pb	466	19%Pb

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	MgSn	200	91%Sn	561	11%Sn
	MgTi	203	80%Ti	353	43%Ti
	PbPd	265	90%Pb	454	61%Pb
	PbPt	290	95%Pb		
5	PbSb	252	18%Sb		
	PbSn	183	26%Pb		
	SbTi	195	30%Sb		
	SeTi	172	73%Se	284	43%Se
	SnTi	170	69%Sn		
10	SnZn	198	85%Sn		

Two particular embodiments BiIn (with 53 % Bi) and BiSn (with 43 % Bi) will be used as the particular embodiments in the detailed descriptions of the following figures. However any materials for the multilayer resist which from alloys that have melting temperatures below that of the individual layers (as do the binary alloys in the chart) form good candidates for this class of thermal resist For the etching requirement, alloys which contain significant percentages of both source materials give superior results. Some particularly interesting other embodiments are BiIn (22 % Bi), notable for its very low conversion temperatures (72°C), and InSn (47 % Sn) for its good compatibility with silicon fabrication processes.

Table I does not include resists where one or more layers is itself a compound material (especially including oxides, nitrides or hydrides) which combine with another layer in the resist to produce more complex compounds. In addition multilayer films, whose alloyed materials combine with oxygen, nitrogen or hydrogen from the surrounding atmosphere are not given as examples here but appear to form some interesting alloys with good resist characteristics. Also it is clear that more than two layer films, forming more complex alloys, can create resists that are useful in some applications. In the detailed descriptions of the figures only two layer resists are discussed although this invention also extends to embodiments which have three or more layers.

In addition to the low temperature eutectic point the layers, should show desired thermal and optical characteristics. Both layers should have a sufficiently low thermal conductivity that the heated area does not create temperatures in

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adjacent areas which exceed the threshold temperature during or after exposure (the exposure may be provided, for example, by a laser pulse). This determination should be made bearing in mind that a typical exposure system exhibits some pulse to pulse variation in exposures and thus will generally be set to provide exposures greater than the applicable threshold levels to produce uniform results. The area over which the heat would spread will determine the resolution available with the resist. For current applications a resolution of better than 0.1 microns is preferred. In addition lower thermal conductivity is advantageous because less energy needed to heat the local area above the thermal reaction point where the thermal conductivity is low.

Figures 1A to 1D illustrate, in simplified form, intermediate steps in the deposition of a thermal inorganic multilayer resist according to one embodiment of the invention. In Figure 1A the process starts with the wafer or device to be processed, which comprises a substrate 4 which may have been processed with lithography in previous operations and a layer 5 that is to be patterned. In one embodiment substrate 4 could comprise a silicon wafer and layer 5 could be a thermal oxide grown on substrate 4. However in some applications the substrate 4 may be defined directly by the resist and no layer 5 will exist.

In Figure 1B a resist protection layer 1 is deposited on top of the substrate layer 5 which is to be patterned. In one embodiment resist protection layer 1 comprises an amorphous carbon film of between 0.2 and 1.0 microns thickness. Preferred deposition processes are dry procedures such as sputter coating, chemical vapour deposition (CVD) or evaporation. In a less desirable process, an organic polymer, such as a standard photoresist, of similar thickness may be used for resist protection layer 1.

As shown in Figure 1C a resist bottom layer 2 is then deposited. This is preferably done using a dry process such as sputtering or CVD. In one embodiment layer 2 comprises an indium film of between 5 and 200 nm thick and, in a specific example, 15 nm thick.

As shown in Figure 1D, a resist top layer 3 is then deposited on top of layer 4. Once again, this is preferably done by a dry process such as sputtering or CVD. Preferably both resist layers 2 and 3 are done in the same deposition system without being exposed to the atmosphere between deposits. In one embodiment layer 3

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comprises a Bismuth film of between 5 and 200 microns thick. The thickness of resist top layer 3 is chosen such that the percentage ratio of the amount of material in layer 3 to the amount of material in layer 2 will yield a desired alloy when the materials are melted together.

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In the case of one BiIn alloy embodiment this requires approximately equal thicknesses for both layers 2 and 3. In a specific example the indium film of layer 2 and the bismuth film of layer 3 are each about 15 nm thick (the deposition control will probably not allow the exact ratio of 53 % Bi).

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Figures 2A through 2C illustrate intermediate stages during the application of an inorganic thermal resist similar to that of Figure 1 but with the thermally active layers deposited directly on the layer 5 which is to be defined (Figure 2A). The process illustrated in Figures 2A through 2C does not include the deposition of a resist protection layer 1 (Fig. 1B). In this embodiment the deposition of the resist bottom layer Figure 2B proceeds using the processes described for Figure 1C. Figure 2C shows the next step, the deposition of the top resist layer 3 using the processes described for Figure 1D. A resist applied as shown in Figures 2A through 2C can be used, for example, in the creation of photomasks for the definition of very thin layer 5 which is to be etched.

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Figure 3 illustrates in simplified form one embodiment of the process steps used to pattern a layer 5 with a thermal inorganic resist deposited as shown in Figure 1. Figure 3A shows a simplified version of the exposure process and equipment. A light source 20, typically a UV laser, produces high power UV light pulse that is expanded by a lens system 21 into a uniform light illumination onto a photomask 22. Photomask 22 contains a pattern to be projected on the wafer (1-5), usually at a larger scale than the final desired pattern. The photomask contains a pattern of dark portions 22A that block light and clear portions 22B which transmit the UV pulses. Lens system 23 then focuses the image from photomask 22 onto the surface of the top resist layer 3 creating image 24 of the mask transmitting portions 22B.

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In most exposure systems this projected image 24 is shrunk relative to the mask pattern 22B by 5 or 10 times, which increases the effective power density of the light at the resist surface. This focused light penetrates the surface of the resist depositing energy in both the top layer 3 and bottom layer 2. The absorbed light

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thermally heats the resist, increasing the temperature above the reaction threshold. In the BiIn resist embodiment the 110°C alloying temperature makes the resist responsive to low light levels. In the preferred embodiment because the eutectic melting temperature is well below the melting temperature of the material of top resist layer 3 the alloy begins to form at the interface between layers 2 and 3. The alloy forms a molten layer that rapidly expands into top and bottom resist layers. The temperature of the unalloyed layers will, in some areas, exceed that of the eutectic point making for a rapid advance of this melt front into the heated illuminated area 10. The eutectic alloy will advance only slowly into any non-illuminated resist.

The result is an alloyed area 10 within unexposed resist that still consists of the separate layers 2 and 3. Thinner layers take less exposure energy to cause the alloying to occur so that films of less than a total thickness of 70 nm (35 nm of Bi and 35 of In in one embodiment) usually provide the most sensitivity. Less desirably, but still useful if the resist thickness is too large or for some resist materials, the process may occur by melting the top resist layer 3 down to the interface, at which point the alloying begins. In one embodiment 150 nm Bi and In layers fuse into a 300 nm thick BiIn alloy area at exposure levels greater than 40mJ/sq cm for 3 nsec pulses from a Nd:Yag laser running at the 4th harmonic of 266 nm and indicate 4 mJ/sq. cm for 15 nm Bi and In layers. It is also possible, as noted, that with some materials oxidation, nitridation or the formation of hydrides of the alloy may occur with the local atmosphere or with gases trapped in the film.

Figure 3B shows the resist after exposure, with the alloyed areas 10 replicating the pattern of the mask 22. These alloyed areas 10 in some materials have very different optical characteristics from the top resist layer 3 making the image directly observable after exposure. In the case of a BiIn resist the films change from highly absorbing to nearly transparent. In particular BiIn resist described in relation to Figure 1 with 15 nm per layer films shows measured transmission changing from <7% in the unexposed areas to >50% and up to 95% (depending on the exposure conditions) in the near UV to visible light range (350 – 700 nm). BiSn thermal resist films also show a tendency to transparency after exposure (although this may be due to oxidation).

Thicker films (200 nm) were measured with transmission less than 0.1%. Such changes in optical parameters allow the wafer to be inspected for defects. As



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the alloying processes is commonly not affected by repeated exposures this allows a resist to be re-exposed to correct low exposures or problems. Indeed as the image is observable the alignment of a re-exposure pattern can be to the exposed pattern and not to structures on the layer 5 or below, which gives better results. In addition the electrical conductivity of the alloyed areas were found to range from the same to 3 times larger than the unexposed areas. This means the transparent film may be conductive, which has important considerations for some types of etching.

Figure 3C illustrates the wafer after a development etch. The etching process, either wet or dry (plasma or reactive ion etching) is used to remove the unexposed layers 2,3 while only slowly attacking the alloyed layer 10. In the particular embodiment of the BiIn resist a wet etch of  $\text{HNO}_3$  (70% solution):  $\text{CH}_3\text{COOH}$  : water in the ratio 1:3:6 will etch away the Bi and In layers 2,3 while reducing alloyed areas 10 by less than 30%. The etchants chosen must be compatible with the resists and alloys used.

In some cases a small amount of alloy will form at the interface during deposition and this will leave small grains of a remnant material after the etching. Such remnant alloy can be removed with a less etching version of the resist stripping process. In the particular embodiment of a BiIn resist a dilute RCA 2 strip of  $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  in the ratio 1:1:48 at room temperature has proved effective in remove these remnants.

Figure 3D illustrates the development etch of the protection resist layer 1 which replicates the image of the thermal resist alloyed pattern 10 into the protection resist. Preferentially an anisotropic etch, such as a plasma or reactive ion etch, is used to get the best pattern transfer. In one particular embodiment with an amorphous carbon protection layer 1 an oxygen plasma etch will remove the carbon not protected by the alloyed resist areas 10. The purpose of the protection resist is two fold. It provides a thicker resist area than the thin thermal resist for etching processes that may attack the resist (for example ion milling). Secondly, it may be desirable to use etching processes of types which will attack the thermal resist for etching certain layer 5 materials. At the same time the thermal resist layer provides protection to etches that would attack the protection layer 1, such as oxygen plasma. Using a protective resist layer 1, in one embodiment an amorphous carbon layer, combined with the protection of the thermal resist layer will provide good resist to almost all plasma etches.

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Figure 3E illustrates the result after etching the layer 5 with the correct etch for that layer, and thus transferring the pattern from the thermal resist alloyed area 10 to the layer 5. Preferably this is done with a dry plasma or reactive ion etch. In one embodiment, where layer 5 is a thermal silicon oxide (glass), a fluorine containing plasma, such as  $\text{CF}_4$ , may be used to etch the glass down to the silicon substrate 4 while only slightly attacking the thermal resist layers.

Figure 3F shows a first resist stripping step where the thermal resist pattern 10 is removed. This may be done by processes such as wet etches or dry etches or ion milling (as the thermal resist layer is so thin). In the particular case of the BiIn resist a wet etch which is identical to the standard RCA clean (RCA 2 or  $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  in the ratio 2:3:14 at  $80^\circ\text{C}$ ) has proved effective in stripping the alloyed resist. This RCA clean is already commonly used in microfabrication processes.

Following the thermal resist strip the protection layer 1 is stripped in Figure 3G. In the particular embodiment of an amorphous carbon protection layer an oxygen plasma is very effective. Note depending on the processes used it may be best to reverse these last two processes stripping the protection layer first and then removing the thermal resist in cleanup operation. In the particular embodiment of the BiIn and carbon films an oxygen plasma etch could be followed by the RCA2 wet etch as a clean up.

Figures 4A through 4D illustrate intermediate stages in the patterning of a layer 5 by a similar process to that of Figures 3A through 3G but with the resist directly deposited on the wafer as in Figure 2C. Thus the resist exposure of Figure 4A is similar to that of Figure 3A but may involve different illumination levels due to the thermal flow to layer 5. The patterned wafer is etched in Figure 4B as described in 3C, and the layer 5 patterned in Figure 4C as described in Figure 3E. Then the resist is stripped in Figure 4D as described in Figure 3F.

Figures 5A and 5B illustrate a laser direct write process. In Figure 5A a laser source 40 is focused by a lens system 41 onto the top of thermal resist layer 3. The resulting laser spot 42 exposes and heats the resist locally creating a small alloyed area 10. The laser can be scanned over the resist surface and its intensity controlled with position to create a laser directly written pattern. Such direct write systems can be used to create specially patterned lithography layers or to write masks. After patterning the wafer is etched as described in relation to Figure 3C to

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yield a resist pattern as shown in Figure 5B. It is possible to do all the steps of Figure 3 in the same manner but with a direct write laser.

Figure 6 illustrates optical characteristics of the films that should be considered to determine the combined layer thickness and the order of the layers. Figure 6 illustrates the optical behaviour of a resist having an In layer 2, and a Bi layer 3 of equal thickness at 248 nm wavelength as a function of the combined thickness of resist layers 2 and 3. Figure 6 shows the variation with the total resist thickness of layer 2 and 3 of the reflection (curve 60) from Bi layer 3, the transmitted light (curve 61) out of the lower edge of bottom In layer 2, and the absorption (curve 62) of energy in the combined resist layers.

The choice of which material to be used in top layer 3 may be made to yield a minimum reflection and maximum absorption using curves like that of Figure 6. The curves of Figure 6 may be generated using the known optical indices of refraction and absorption indices at the desired wavelengths for the materials to be used in layers 2 and 3. As many materials suitable for use in layers 2 and 3 are highly absorbing metals these curve calculations must be done using optical multilayer thin film analysis including complex indexes and the effects of internal reflection using well known methods to practitioners of the art. For metal layer resists these optical characteristics result in modestly more energy being deposited in the resist at shorter wavelengths. Thus the optical exposure threshold only changes modestly from UV at 350 nm to the deep UV at 150 nm or shorter.

Since the metals, unlike organics, do not tend to suffer photoablation at wavelengths for modest exposures in the 150 to 250 nm range this makes them good candidates for the deep UV resists desired for advanced lithographic images. For lithographic resists the reflection from the film surface should be minimized but the transmission of light from the lower layer is not to important. However in other applications, like the generation of photomasks, the transmitted light of curve 61 out of the bottom layer 2 should be below some value. This may require thicker films. In one embodiment to get a transmission of less than 0.1% for Bi on In resist, each layer should be 35 nm thick (as illustrated by the curves of Figure 6. Such thicker films will be less optically sensitive, but provide better blocking of light in unexposed areas.

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For increased protection an overcoating layer can be added to the photomask on top of the active layers. Such a protective transparent overcoat may comprise a cross-linked organic material or an inorganic layer, typically silicon dioxide.

5           Figure 7 illustrates the energy  $Q$  (curve 70) deposited per unit volume (W/cc) by light as it varies in intensity passing through a resist. The curve 70 of Figure 7 is for the example of a resist comprising an In layer 2 of 15 nm thickness and a Bi layer 3 of 15 nm, for illumination at 248 nm wavelength. The bottom of layer 2 corresponds to a distance of 0 nm. The portion of  $Q$  curve 70 labelled 72 is  
10 the energy deposited in the bottom layer 2, while the portion of  $Q$  curve 70 labelled 73 represents energy deposition in top resist layer 3. Total film thicknesses are best when the optical energy absorption rate  $Q$  allows energy deposition in both film layers. Note the sudden drop of the  $Q$  energy deposition at the BiIn interface, point  
15 71 (15 nm thickness).

With longer wavelengths or different materials the  $Q$  rate will be higher in the bottom layer 2 (In) near the interface then at the top of the top layer 3 (Bi) just above the interface 71. These calculations are done using Poynting Vector analysis, including the effects of internal reflections, using methods well-known to  
20 practitioners of the art. In general the actual energy  $Q$  deposited in the film per unit volume increases as thickness decreases. Since a higher  $Q$  results in greater temperatures for a given illumination level, and especially higher temperatures at the interface, this creates more sensitivity thinner films, especially for total film thicknesses less than 70 nm.

25           Note that the ability of the BiIn resist to become transparent with exposure suggests that it can be directly used with a direct write laser system as in Figure 5 to produce photomasks without etching the resist. Depending on the exposure levels and film thickness, BiIn alloys show transparency in the UV to wavelengths as short  
30 as 350 nm before absorption begins to rise. In resists using other materials this transmission may extend to shorter wavelengths. For use at wavelengths in which the exposed resist does not transmit, a resist development and etch process can be used to create masks. In either case this should create masks with fewer defects than standard techniques which involve photoresist application and stripping. This  
35 direct writing of images on resist films suggests these same materials may be useful for optical information storage.

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Some phase diagrams show more than one phase material ratio with temperatures below the individual layer melting points. Thus when heated by optical exposures that create temperatures in the film above the eutectic point the films begin to alloy at the interface between the layers. Since the alloy has a lower melting point than either individual film this reaction will occur at a much lower temperature than the melting or vaporization temperatures of the individual films. None of the films tested show ablation of the materials after exposure at levels near the threshold. The ratio of the film thicknesses should be such that when fully combined the resulting alloy will near the desired composition. Since current laser optical UV microlithographic exposure systems involve very short pulses (about 20 nsec or less) the relatively low average energy of exposure actually involves very high instantaneous optical powers during a single pulse (10 mJ per square cm in 20 nsec. is 0.5 megawatts of power per square cm during the pulse). Such high powers drive the alloying process if the film is thin enough.

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the spirit or scope thereof. Accordingly, the scope of the invention is to be construed in accordance with the substance defined by the following claims.

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WHAT IS CLAIMED IS:

1. A thermal inorganic resist comprising:
  - a) a first layer of a first material on a substrate;
  - b) a second layer of a second material on the first layer;characterized by the first and second materials have a eutectic alloy and the first and second layers have thicknesses such that alloying the materials in the first and second layers results in a composition near that of the eutectic alloy.
2. The thermal inorganic resist of claim 1 comprising a protective layer between the first layer and the substrate.
3. The thermal inorganic resist of claim 2 wherein the protective layer comprises an amorphous carbon material.
4. The thermal inorganic resist of any of claims 1 to 3 wherein the first and second materials comprise a pair of metals.
5. The thermal inorganic resist of claim 4 wherein the pair of metals is selected from the group consisting of the pairs AsPb, BiCd, BiCo, BiIn, BiPb, BiSn, BiZn, CdIn, CdPb, CdSb, CdSn, CdTi, CdZn, GaIn, GaMg, GaSn, GaZn, InSn, InZn, MgPb, MgSn, MgTi, PbPd, PbPt, PbSb, PbSn, SbTi, SeTi, SnTi, and, SnZn.
6. The thermal inorganic resist of claim 4 wherein the pair of metals is BiIn.
7. The thermal inorganic resist of claim 4 wherein the eutectic alloy has a melting point of less than 300°C.
8. A method of creating an inorganic thermal resist, the method comprising:
  - a) depositing a first layer of an inorganic thin film on a substrate;
  - b) depositing one or more layers of another inorganic material or materials on the first layer;
  - c) imagewise exposing the layers to create a resultant material with different etching characteristics from any of the layers of unexposed materials.

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9. A method according to claim 8 wherein the resultant material has optical transmission characteristics different from any of the unexposed materials.
- 5 10. The method of claim 8 wherein the resulting material has optical characteristics different from any of the unexposed materials thus creating a visible image on a surface of the resist which can be viewed by simple illumination with optical radiation.
- 10 11. A method for creating an inorganic thermal resist, the method comprising:  
a) depositing a first layer of an inorganic thin film on a substrate;  
b) depositing one or more additional layers of another inorganic material or materials on the first layer;  
c) imagewise exposing the layers to create a resultant material with a melting point below those of the materials of the first layer and one  
15 or more additional layers.
12. A method according to claim 11 wherein the resultant material has optical transmission characteristics different from any of the unexposed materials.
- 20 13. The method of claim 11 wherein the resulting material has optical characteristics different from any of the unexposed materials thus creating a visible image on a surface of the resist which can be viewed by simple illumination with optical radiation.
- 25 14. A method for creating an inorganic thermal resist, the method comprising:  
a) depositing a first layer of an inorganic thin film on a substrate;  
b) depositing one or more additional layers of another inorganic material or materials on the first layer;  
c) imagewise exposing the layers, to create a resultant which is a  
30 eutectic alloy of the materials of the first layer and one or more additional layers.
15. A method according to claim 14 wherein the resultant material has optical transmission characteristics different from any of the unexposed materials.
- 35 16. The method of claim 14 wherein the resulting material has optical characteristics different from any of the unexposed materials thus creating a

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visible image on a surface of the resist which can be viewed by simple illumination with optical radiation.

- 5 17. The method of claim 14 wherein the eutectic has a melting point below 300 degrees Celsius.
18. The method of claim 14 wherein the eutectic contains at least 5 percent of one of the unexposed materials.
- 10 19. A method for creating an inorganic thermal resist, the method comprising:
- a) depositing a first layer of an inorganic thin film on a substrate;
  - b) depositing one or more additional layers of another inorganic material or materials on the first layer;
  - 15 c) imagewise exposing the layers, the exposure causing a reaction with surrounding gases to create a resultant material comprising oxides, nitrides or hydrides of an alloy of the materials of the first layer and one or more additional layers, the resultant material having different etching characteristics from any of said layers of unexposed materials.
- 20 20. A method according to any one of claims 8 to 19 wherein the unexposed materials are metals.
- 25 21. A method according to any one of claims 8 through 20 wherein the imagewise exposing is performed with directed radiation having wavelengths in the range from 10 nm to 100 microns.
- 30 22. A method according to any one of claims 8 through 20 wherein the imagewise exposing is performed with a directed particle beam of electrons or ions.
- 35 23. A method according to any one of claims 8 through 22 wherein the resultant material comprises a binary alloy selected from the group consisting of: AsPb, BiCd, BiCo, BiIn, BiPb, BiSn, BiZn, CdIn, CdPb, CdSb, CdSn, CdTl, CdZn, GaIn, GaMg, GaSn, GaZn, InSn, InZn, MgPb, MgSn, MgTl, PbPd, PbPt, PbSb, PbSn, SbTl, SeTl, SnTl, and, SnZn.



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24. A photomask material comprising of at least two layers of thin inorganic coatings, said coatings changing from opaque to transparent when heated made by any of the methods of claims 8 to 23.
- 5 25. A photomask material comprising of at least two layers of thin inorganic coatings, said coatings changing from opaque to transparent when heated.
26. The photomask of claim 25 comprising a transparent protective overcoat.
- 10 27. The photomask of claim 26 wherein the overcoat comprises a cross-linked polymer.
28. A method for providing an imaged mask on a substrate, the method comprising:
- 15 a) providing on the substrate adjoining layers of at least a first material and a second material; and
- b) imagewise heating selected areas of the layers and thereby causing the layers to melt together to form a eutectic alloy of the first and second materials in the selected areas.
- 20 29. The method of claim 28 wherein the first and second material are metals.
30. The method of claim 29 wherein the imagewise heating comprises irradiating the selected areas with a beam of radiation.
- 25 31. The method of claim 30 wherein the first and second areas have thickness such that the irradiating deposits substantial energy in each of the adjoining layers.

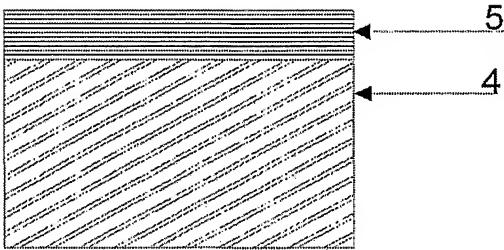


FIG.1A

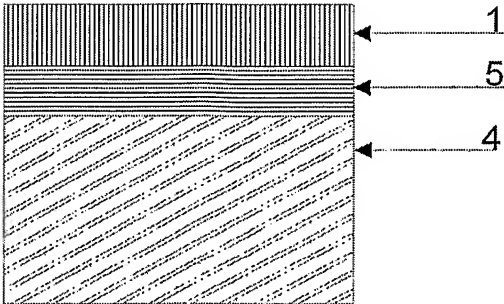


FIG.1B

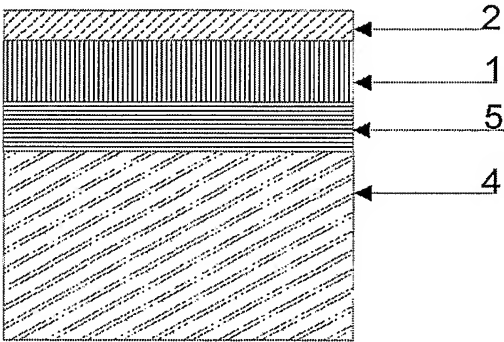


FIG.1C

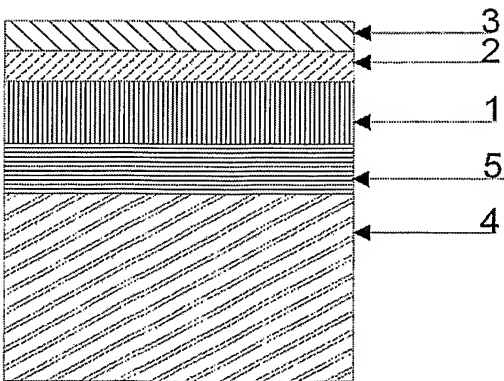


FIG.1D

FIG.1

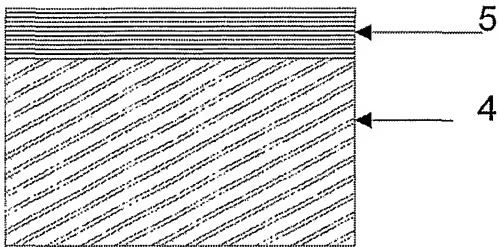


FIG.2A

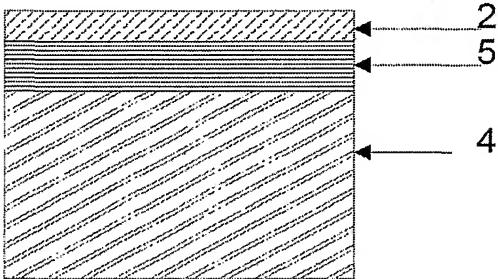


FIG.2B

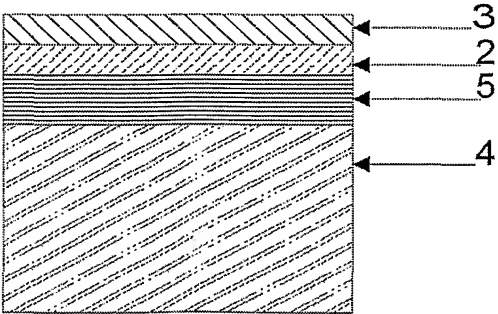


FIG.2C

FIG.2

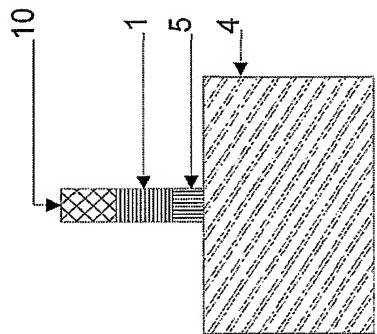


FIG. 3E

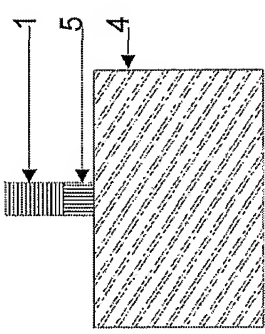


FIG. 3F

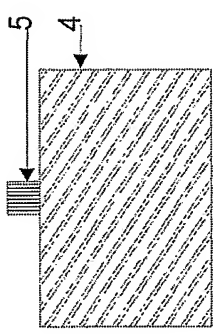


FIG. 3G

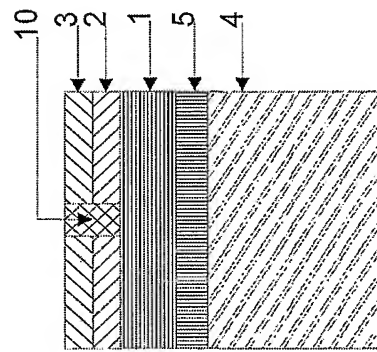


FIG. 3B

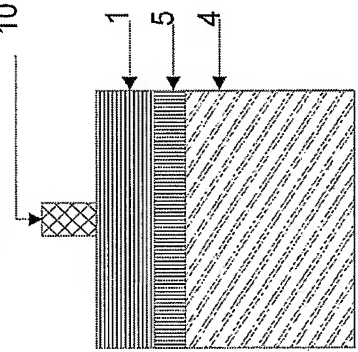


FIG. 3C

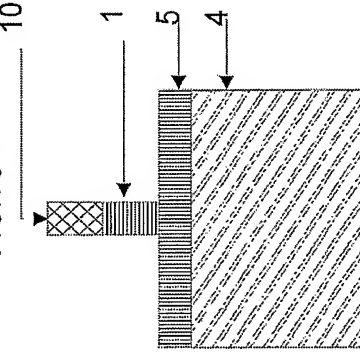


FIG. 3D  
FIG. 3

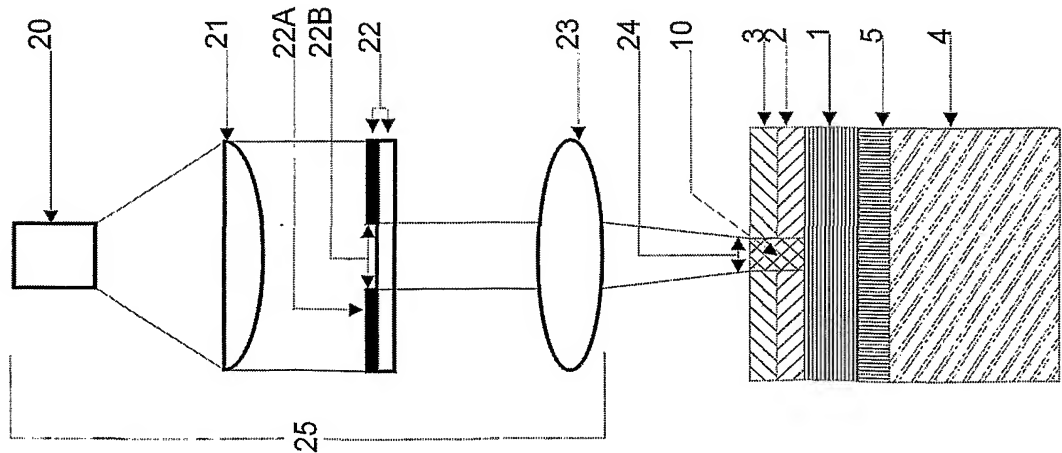


FIG. 3A

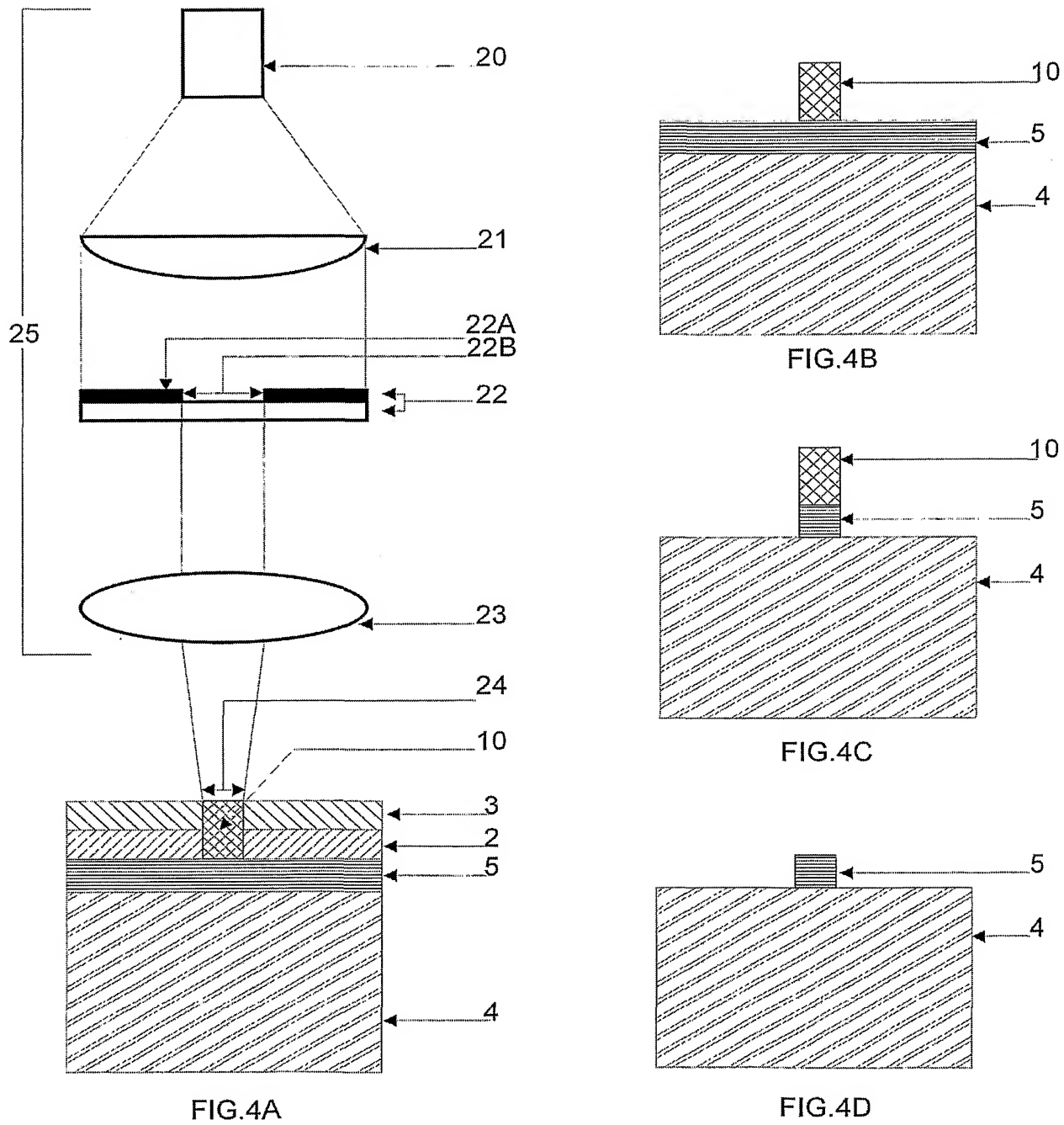


FIG. 4

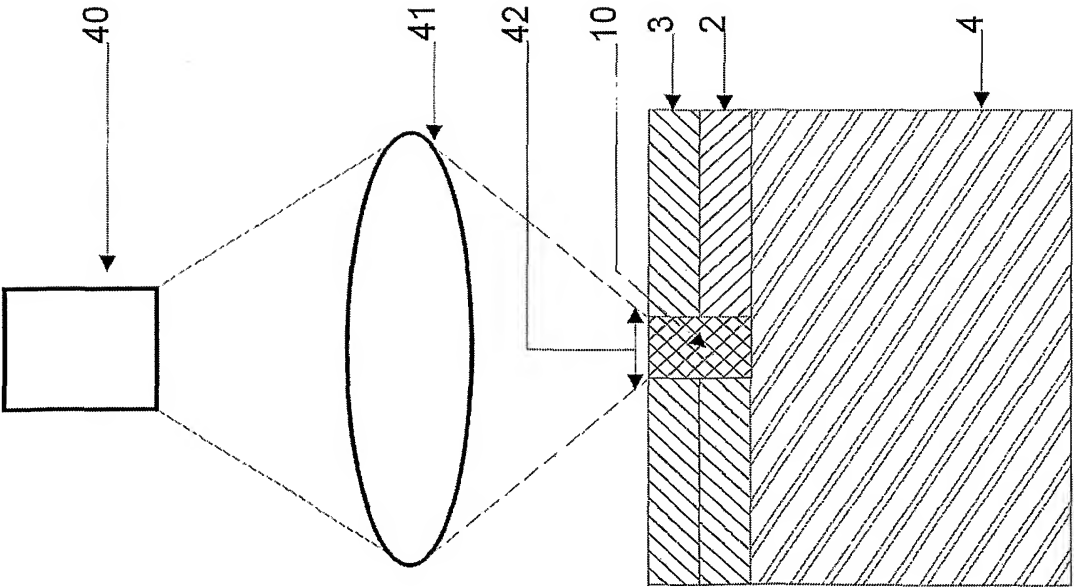


FIG. 5A

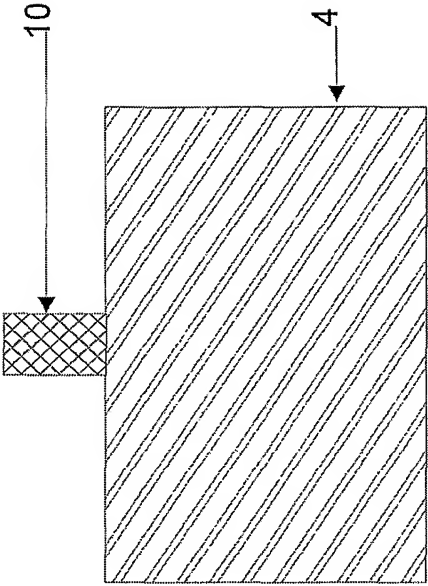


FIG. 5B

FIG. 5

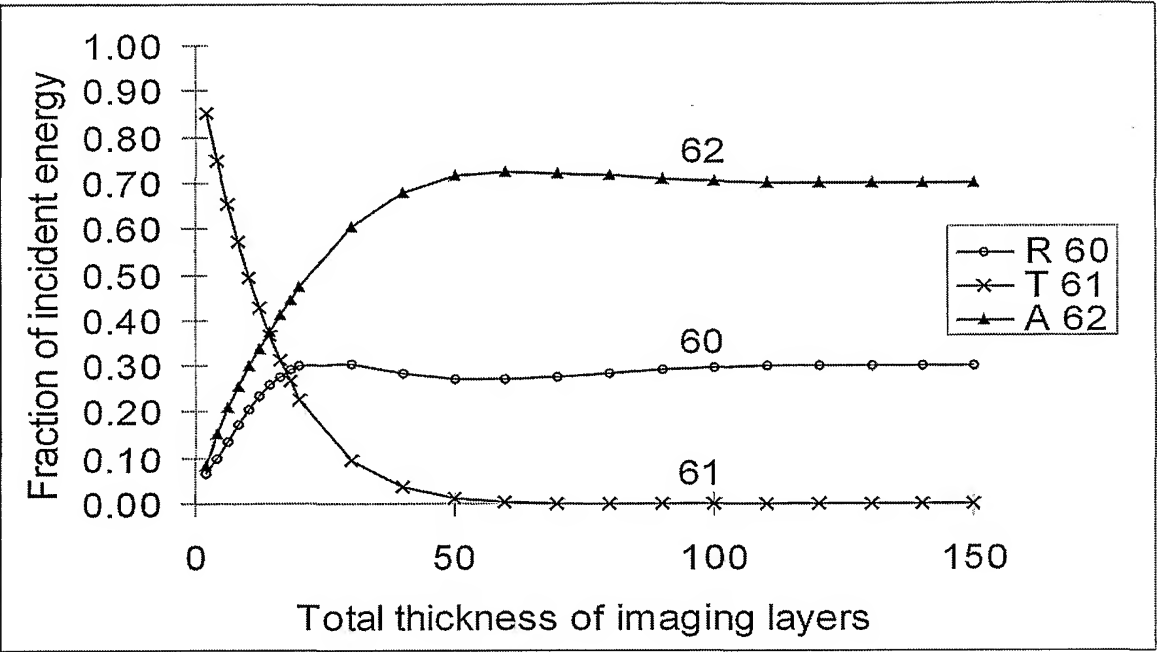


FIG. 6

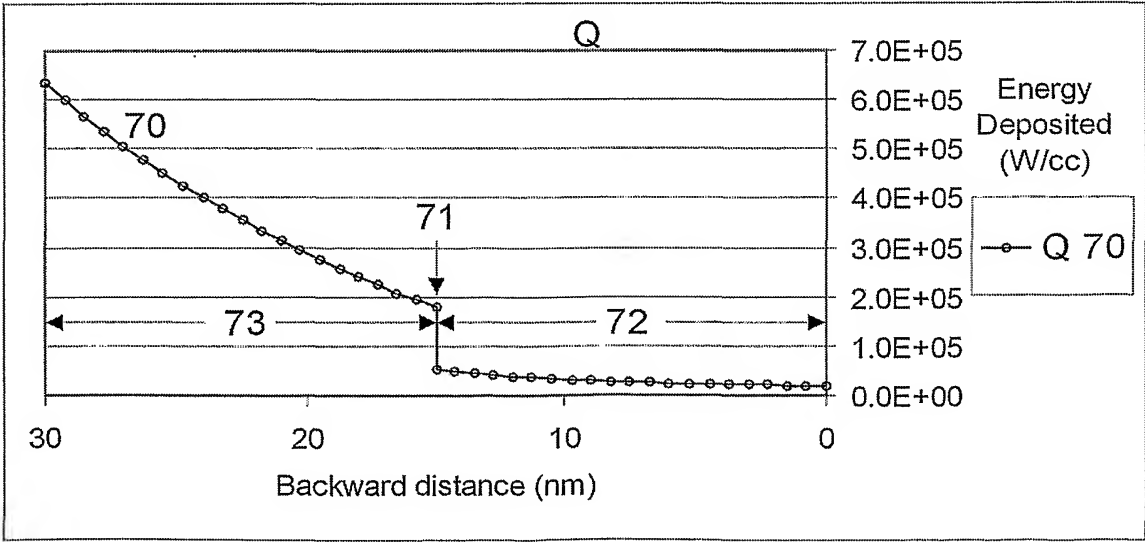


FIG. 7